



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the Application of

Jacques Hubert Olga Joseph WIJENBERG et al.

Serial No.: 10/621,601

Examiner: J. Combs-Morillo

Filed: July 18, 2003

Art Unit: 1775

For: BRAZING PRODUCT AND METHOD OF MANUFACTURING A BRAZING PRODUCT

**CLAIM FOR PRIORITY**

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Sir:

The benefit of the filing date of the following prior foreign application filed in the following foreign country is hereby requested for the above-identified application and the priority provided in 35 USC 119 is hereby claimed:

European Patent Application No. 02078054.0 filed July 24, 2002.

A certified copy of this priority document is enclosed. It is requested that the file of this application be marked to indicate that the requirements of 35 USC 119 have been fulfilled and that the Patent and Trademark Office kindly acknowledge receipt of this document.

Respectfully submitted,

Date:

May 23, 2005

By:

Anthony P. Venturino

Anthony P. Venturino

Registration No. 31,674

APV/bms

ATTORNEY DOCKET NO. APV31637

STEVENS, DAVIS, MILLER & MOSHER, L.L.P.  
1615 L Street, N.W., Suite 850  
Washington, D.C. 20036  
Tel: 202-408-5100 / Fax: 202-408-5200

***This Page Blank (uspto)***



**Europäisches  
Patentamt**

**European  
Patent Office**

**Office européen  
des brevets**

**Bescheinigung**

**Certificate**

**Attestation**

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.

The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

**Patentanmeldung Nr.    Patent application No.    Demande de brevet n°**

02078054.0

Der Präsident des Europäischen Patentamts;  
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets  
p.o.

**R C van Dijk**

***This Page Blank (uspto)***



Anmeldung Nr:  
Application no.: 02078054.0  
Demande no:

Anmeldetag:  
Date of filing: 24.07.02  
Date de dépôt:

Anmelder/Applicant(s)/Demandeur(s):

Corus Technology BV  
P.O. Box 10000  
1970 CA Ijmuiden  
PAYS-BAS

Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:  
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.  
If no title is shown please refer to the description.  
Si aucun titre n'est indiqué se référer à la description.)

Brazing product and method of manufacturing a brazing product

In Anspruch genommene Priorität(en) / Priority(ies) claimed /Priorité(s)  
revendiquée(s)  
Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation/International Patent Classification/  
Classification internationale des brevets:

B23K35/00

Am Anmeldetag benannte Vertragstaaten/Contracting states designated at date of  
filing/Etats contractants désignées lors du dépôt:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR IE IT LI LU MC NL PT SE SK TR

**This Page Blank (uspto)**

## BRAZING PRODUCT AND METHOD OF MANUFACTURING A BRAZING PRODUCT

### FIELD OF THE INVENTION

5       The invention relates to a sheet brazing product and to a method of manufacturing an Al or Al alloy workpiece, such as a brazing sheet product, comprising the steps of providing an Al or Al alloy workpiece, pre-treating of the outersurface of the Al or Al alloy workpiece, and plating a metal layer comprising nickel onto the outersurface of the pre-treated workpiece. The invention also relates  
10   to a brazed assembly comprising at least one component made of this brazing product manufacturing according to this invention.

### DESCRIPTION OF THE RELATED ART

Aluminium and aluminium alloys can be joined by a wide variety of brazing and soldering processes. Brazing, by definition, employs a filler metal or alloy  
15   having a liquidus above 450°C and below the solidus of the base metal. Brazing is distinguished from soldering by the melting point of the filler metal: a solder melts below 450°C. Soldering processes are not within the field of the present invention.

Brazing products, and in particular brazing sheet products, find wide applications in heat exchangers and other similar equipment. Conventional brazing  
20   sheet products have a core or base sheet, typically an aluminium alloy of the Aluminium Association ("AA") 3xxx-series, having on at least one surface of said core sheet clad an aluminium clad layer, the aluminium clad layer being made of an AA4xxx-series alloy comprising silicon in an amount in the range of 4 to 14% by weight, and preferably in the range of 7 to 14% by weight. The aluminium clad layer  
25   may be coupled to the core or base alloy in various ways known in the art, for example by means of roll bonding, cladding, explosive cladding, thermal spray-forming or semi-continuous or continuous casting processes.

Controlled Atmosphere Brazing ("CAB") and Vacuum Brazing ("VB") are the two main processes used for industrial scale aluminium brazing. Industrial vacuum  
30   brazing has been used since the 1950's, while CAB became popular in the early 1980's after the introduction of the NOCOLOK (trade mark) brazing flux. Vacuum brazing is an essentially discontinuous process and puts high demands on material cleanliness. The disruption of the aluminium oxide layer present is mainly caused by

- 2 -

the evaporation of magnesium from the clad alloy. There is always more magnesium present in the furnace than necessary. The excess magnesium condenses on the cold spots in the furnace and has to be removed frequently. The capital investment for suitable equipment is relatively high.

5 CAB requires an additional process step prior to brazing as compared to VB, since a brazing flux has to be applied prior to brazing. A brazing flux for use in brazing aluminium alloys usually consist of mixtures of alkali earth chlorides and fluorides, sometimes containing aluminium fluoride or cryolite. CAB is essentially a continuous process in which, if the proper brazing flux is being used, high volumes  
10 of brazed assemblies can be manufactured. The brazing flux dissolves the oxide layer at brazing temperature allowing the clad alloy to flow properly. When the NOCOLOK flux is used the surface needs to be cleaned thoroughly prior to flux application. To obtain good brazing results the brazing flux has to be applied on the total surface of the brazed assembly. This can cause difficulties with certain types of  
15 assemblies because of their design. For example, because evaporator type heat exchangers have a large internal surface, problems can arise because of poor access to the interior. For good brazing results the flux has to adhere to the aluminium surface before brazing. Unfortunately the brazing flux after drying can easily fall off due to small mechanical vibrations. During the brazing cycle, corrosive fumes such  
20 as HF are generated. This puts a high demand on the corrosion resistance of the materials applied for the furnace.

Ideally, a material should be available that can be used for CAB but does not have the requirements and defects of the known brazing flux application. Such a material can be supplied to a manufacturer of brazed assemblies and is ready to use  
25 directly after forming of the assembly parts. No additional brazing fluxing operations have to be carried out. Presently, only one process for fluxless brazing is used on an industrial scale. The material for this process can be for example standard brazing sheet made from an AA3xxx-series core alloy clad on one or both sides with a cladding of an AA4xxx-series alloy. Before the brazing sheet can be used the surface  
30 has to be modified in such a way that the naturally occurring aluminium oxide layer does not interfere during the brazing cycle. The method of achieving good brazing is to deposit a specific amount of nickel on the surface of the clad alloy. If properly



- 3 -

applied, the nickel reacts, presumably exothermically, with the underlying aluminium. When electroplating is used the adherence of the nickel should be sufficient to withstand typical shaping operations being used in for example heat exchanger manufacture.

5 Processes for nickel-plating in an alkaline solution of aluminium brazing sheet are known from each of US-A-3,970,237, US-A-4,028,200, and US-A-4,164,454. According to these documents, nickel or cobalt, or combinations thereof, are most preferably deposited in combination with lead. The lead addition is used to improve the wettability of the aluminium clad alloy during the brazing cycle. An important  
10 characteristic of these plating processes is that the nickel is preferentially deposited on the silicon particles of the aluminium clad alloy. To obtain sufficient nickel for brazing, the surface of the aluminium clad alloy should contain a relatively large number of silicon particles to act as nuclei for the nickel deposition. It is believed that to obtain sufficient nucleation sites a part of the aluminium in which the silicon  
15 particles are embedded should be removed before pickling by chemical and/or mechanical pre-treatment. This is believed a necessary condition to obtain sufficient silicon coverage to serve as nuclei for the plating action of the brazing or clad alloy. On a microscopic scale the surface of the Si-containing cladding of the brazing sheet is covered with nickel-lead globules. However, the use of lead for the production of a  
20 suitable nickel and/or cobalt layer on brazing sheet has several disadvantages. The use of lead for manufacturing products, such as automotive products, is undesirable and it is envisaged that in the very near future there might possibly even be a ban on lead comprising products or products manufactured via one or more intermediate processing steps comprising lead or lead-based components.

25 The international PCT patent application no. WO-00/71784, of J.N. Mooij *et al.* discloses a brazing sheet product and a method of its manufacture. In this brazing sheet product there is provided a very thin bonding layer, preferably applied by plating, comprising zinc or tin between the AlSi-alloy clad layer and the nickel layer in order to improve the bonding of the nickel layer. The addition of lead to the nickel  
30 layer has been replaced by the addition of bismuth while maintaining the excellent brazeability characteristics of the brazing sheet product.

A drawback of the known brazing sheet products having a layer comprising

- 4 -

nickel is the limited corrosion life of brazed products in a SWAAT-test in accordance with ASTM G-85. Post-braze corrosion lifetimes without perforations are typically in the range of 4 days and thereby restricting possible interesting applications of this brazing product. For several applications of the known nickel-plated brazing sheet in brazed products such a relatively short corrosion lifetime is not detrimental. However, a good corrosion resistance is considered a valuable property for brazing products used in amongst others heat exchangers, such as radiators and condensers. These heat exchangers are exposed to a severe external corrosive attack by e.g. de-icing road salt.

#### 10 SUMMARY OF THE INVENTION

It is an object of the present invention to provide a Ni-plated brazing sheet product for use in a brazing operation, ideally a fluxless CAB brazing operation, and wherein the brazing sheet product has an improved post-braze corrosion resistance when measured in a SWAAT-test in accordance with ASTM-G-85.

15 It is a further object of the present invention to provide a method of manufacturing Ni-plated brazing product for use in a brazing operation, ideally a fluxless CAB brazing operation, and wherein the resultant brazing product has an improved post-braze corrosion resistance when measured in a SWAAT-test in accordance with ASTM G-85.

20 It is another object of the present invention to provide a method of manufacturing a brazing sheet product comprising a core sheet made of an aluminium alloy coupled on at least one surface of said core sheet to an aluminium clad layer, the aluminium clad layer being made of an aluminium alloy comprising silicon in an amount in the range of 4 to 14% by weight, and a further layer  
25 comprising nickel on the outer surface of said aluminium clad layer such that taken together said aluminium clad layer and all layers exterior thereto form a filler metal for a brazing operation, and wherein the resultant brazing sheet product has an improved post-braze corrosion resistance when measured in a SWAAT-test in accordance with ASTM G-85.

30 In accordance with the invention in one aspect there is provided a brazing sheet product having a core sheet, on at least one side of said core sheet a clad layer of an aluminium alloy comprising silicon in an amount in the range of 4 to 14% by weight,

- 5 -

and further comprising on at least one outersurface of said clad layer a plated layer of nickel-tin alloy, such that the clad layer and all layers exterior thereto form a metal filler for a brazing operation and having a composition with the proviso that the mol-ratio of Ni:Sn is in the range of 10:(0.5 to 9), and preferably 10:(0.5 to 6).

5 With the brazing sheet product according to the invention there is achieved a post-braze corrosion lifetimes without perforations according to ASTM G-85 of 6 days or more. The brazing sheet product can be fluxless brazed under controlled atmosphere conditions in the absence of a brazing flux material while achieving improved post-braze corrosion performance enhancing the possibilities of application  
10 of the Ni-plated brazing products.

The invention is based in part on the insight that it is believed that the cathodic reaction governs the overall corrosion rate of Ni-plated brazing products when tested in the SWAAT-test in accordance with ASTM G-85. It is speculated that the cathodic reaction in this system appears to be the Hydrogen Evolution Reaction  
15 ("HER"). When Ni-plated brazing products such as brazing sheets are being subjected to a brazing operation, typically a fluxless CAB operation, small Ni-aluminide particles are being formed which are believed to catalyse the HER. By the addition of tin in a sufficient amount to the metal filler and having a lower exchange current density for the HER as compared to nickel-aluminides the catalyse effect is  
20 reduced and the post-braze corrosion performance of the brazed product is being improved remarkably.

It is believed that an upper layer of pure tin metal is sensitive to progressive oxidation in pre-braze conditions under humid conditions, e.g. during transport of a plated coil to a customer. The surface oxides formed adversely influence the brazing  
25 process. By providing the tin required to improve the post-braze corrosion performance in the form of a plated nickel-tin alloy layer, no free tin is available anymore and thereby avoiding the occurrence of the detrimental progressive oxidation of the tin. It has been found that the plated Ni-Sn alloy layer forms a thin stable surface oxide film in air.

30 The invention in another aspect is characterised by a method of manufacturing an Al or Al alloy workpiece, which method comprises the steps of (a) providing an Al or Al alloy workpiece, (b) pre-treating of the outersurface of the Al or Al alloy

- 6 -

workpiece, and (c) plating a metal layer comprising nickel onto said outersurface of the Al or Al alloy workpiece, and wherein during step (c) said metal layer comprising nickel is deposited by plating a nickel-tin alloy using an aqueous plating bath comprising a nickel-ion concentration in a range of 2 to 50 g/l, and preferably 0.2 to 20 g/l., and a tin-ion concentration in the range of 0.2 to 20 g/l, and preferably 0.2 to 8 g/l.

According to this aspect of the invention there is provided a method of forming an Ni-plated aluminium brazing workpiece, ideally a brazing sheet product, with a plated nickel-tin alloy layer on the workpiece, the plated nickel-tin alloy layer improving the post-braze corrosion performance of the resultant product.

In an embodiment the outersurface of the workpiece in of an AlSi-alloy or an AlSi-alloy clad layer and all layers exterior thereto form a metal filler for a brazing operation and have a composition with the proviso that the mol-ratio of Ni:Sn is in the range of 10:(0.5 to 9), and preferably in the range of 10:(0.5 to 6). When the mol-ratio is too low no significant improvement in the post-braze corrosion life may be found. It has been found that if the mol-ratio becomes more than 10:6, then the brazeability becomes less efficient, while at a mol-ratio of more than 10:9 the brazeability becomes very poor.

In the plating bath used in the method according to the invention the nicle and tin ion concentration is such that the tin ion concentration should be in the range of 5 to 70 wt.%, and preferably in the range of 5 to 30 wt.% in order the arrive at the desired Ni:Sn mol-ratio in the plated layer. The balance in metal ions in made by nickel. Both the tin and nickel ions are preferably added to the plating bath in the form of salts, in particular as chloride salt ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ).

The plating bath preferably comprises sodium pyrophosphate ( $\text{Na}_4\text{P}_2\text{O}_7$ ) or potassium pyrophosphate ( $\text{K}_4\text{P}_2\text{O}_7$ ) as a complexing agent for the metal ions in the bath. The pyrophosphate should be added in the range of 65 to 650 g/l, and preferably 100 to 350 g/l.

In addition to the pyrophosphate there should preferably be present a further complexing agent, preferably a  $\alpha$ -amino acid to obtain a bright, fine-grained deposit. A very practical  $\alpha$ -amino acid is glycine (amino acetic acid:  $\text{NH}_2\text{CH}_2\text{COOH}$ ). Glycine shifts the polarisation curve of nickel towards a more noble potential, while

- 7 -

leaving the polarisation curve of the tin practically unaffected. This further complexing agent should be present in a range of 4 to 50 g/l, preferably 5 to 40 g/l.

The overall balance of the Ni-Sn plating bath used in the method according to the invention, which comprises the components detailed above, is water. When practicing the plating method of the present invention, it is preferred to main the pH value of the plating bath at a level ranging from 6.5 to 9.0 throughout the plating operation, and preferably in the range of 7.5 to 8.5. If the pH value is less than 6.5 or if it exceeds 9, the stability of the metal ions present in the plating bath is significantly reduced.

The plating bath according to the present invention is substantially free of lead ions, and preferably the bath does not comprise any lead ions at all.

The aqueous plating bath demonstrated to be operational in a reasonable pH range, and at a wide temperature range of 30 to 70°C, and preferably 40 to 60°C, and further can be used in industrial scale coil plating lines using current densities up to about 4 A/dm<sup>2</sup>, and preferably using current densities in the range of 0.4 to 3.0 A/dm<sup>2</sup>. At too high current densities coarse deposits are obtained. Further advantages of this plating bath are that it does not generate any ammonia fumes, it does not use any components based on fluorides, it can be composed using standard and readily available chemicals, and the nickel ion and tin ion concentrations can easily be replenished to the plating bath from soluble anodes of these metals.

In a preferred embodiment all the nickel present for the metal filler used in the brazing operation is deposited simultaneously with the tin into a nickel-tin alloy. However, it is possible to firstly electroplate a thin nickel layer or nickel-bismuth layer, or vice versa, for example by using the aqueous Ni-Bi plating bath as set out in the international application WO-01/88226, and incorporated herein by reference, and on the outersurface of this first nickel or nickel-alloy layer there is plated the nickel-tin alloy layer. In the plated nickel-tin alloy layer the tin content should be increased to arrive at the desired Ni:Sn mol-ratio in the metal filler. However, this approach requires an additional plating step, and it is preferred to use one electroplating step only.

In an embodiment taken together said aluminium base substrate and all layers exterior thereto form a metal filler for a brazing operation and having a composition

- 8 -

comprising at least, by weight percent:

Si in the range of 5 to 14 %,

Ni in the range of 0.03 to 8%,

Sn in the range of 0.01 to 7%,

5 Bi in the range of at most 0.3%,

Sb in the range of at most 0.3%,

Zn in the range of at most 0.3%,

Mg in the range of at most 5%,

balance aluminium and inevitable impurities,

10 and with the proviso that the mol-ratio of Ni:Sn is in the range of 10:(0.5 to 9), and preferably in the range of 10:(0.5 to 6). The reasons for the limitations of the Ni:Sn mol-ratio have been set out above.

A typical impurity element in the filler metal is iron, in particular originating from the AlSi-alloy substrate or AlSi-alloy clad layer, and which may be tolerated up  
15 to about 0.8 %. Other alloying elements may be present, and will typically originate from the aluminium base substrate or alternatively the aluminium clad layer. Typically each impurity element is present in a range of not more than 0.05 %, and the total of the impurity elements does not exceed 0.3%.

Preferably the applied layer comprising the nickel-tin alloy has a thickness of at  
20 most 2.0µm, preferably at most 1.0µm, and more preferably in the range of 0.1 to 0.8µm. A coating thickness of more than 2.0µm requires a prolonged treatment time for plating, and may result in wrinkling of the molten filler metal during a subsequent brazing operation. A preferred minimum thickness for this nickel-tin alloy layer is about 0.25µm. Also other techniques such as dipping, thermal spraying, CVD, PVD  
25 or other techniques for depositing of metal alloys from a gas or vapour phase may be used. Preferably the nickel-tin alloy layer is essentially lead-free.

In an embodiment the Al or Al alloy workpiece is an aluminium alloy sheet or aluminium alloy wire or aluminium alloy rod. Although various aluminium alloys may be applied, e.g. those within the Aluminium Association (AA)3xxx- and  
30 AA6xxx-series aluminium alloys, particular suitable aluminium alloys are those within the AA4xxx-series alloys, typically having Si as the most important alloying

element in the range of 4 to 14% by weight, more preferably 7 to 14% by weight. Other alloying elements may be present to improve specific properties, the balance is made by iron up to 0.8%, and impurities each up to 0.05 wt.%, total up to 0.25 wt.%, and aluminium. An AA4xxx-series aluminium alloy sheet can be plated with Ni-Sn alloy in accordance with the method of the invention, and may be employed in subsequent brazing operations, in particular in an inert atmosphere brazing (CAB) operation in the absence of a brazing-flux material. Also aluminium alloy wire or rods being made of an AA4xxx-series alloy may be plated with a Ni-Sn alloy layer, and subsequently employed in brazing operations in particular in an inert atmosphere brazing (CAB) operations in the absence of a brazing-flux material, and may also be employed as weld filler wire or weld filler rod in a welding operation.

In a preferred embodiment the aluminium alloy workpiece is a brazing sheet product comprising a core sheet coupled at least one surface of said core sheet to an aluminium clad layer, the aluminium clad layer being made of an aluminium AA4xxx-series alloy comprising silicon in the range of 4 to 14% by weight, preferably in the range of 7 to 14%.

In an embodiment of said aluminium brazing sheet product, the core sheet is made of an aluminium alloy, in particular those within the AA3xxx, AA5xxx, or AA6xxx-series aluminium alloys.

In a further embodiment the AlSi-alloy clad layer has a thickness ranging from about 2 to 20% of the total thickness of the total brazing product thickness. Typical AlSi-alloy clad layer thickness is in the range of 40 to 80 micron. The aluminium core sheet has a thickness typically in a range of at most 5 mm, more preferably in the range of 0.1 to 2 mm.

In an embodiment of the brazing sheet product it is further characterised by an optional applied thin layer comprising zinc as an intermediate bonding layer between the outersurface of the AlSi-alloy clad layer and said nickel-tin alloy plated layer. With the zinc comprising intermediate bonding layer a very effective bond between the AlSi-alloy clad layer and the nickel-tin layer is formed, the bond remaining effective during subsequent deformation of the brazing product, for example in a bending operation. Preferably the intermediate bonding layer has a thickness of at most 0.5µm, more preferably at most 0.3µm (300nm), and most preferably in the

- 10 -

range of 0.01 to 0.15 $\mu$ m (10-150nm). In the best results obtained a thickness of about 30nm has been used. It has been found that the thin bonding layer of zinc has no detrimental effect on the post-braze corrosion performance of the brazing product according to the invention.

5       The adhesion of the Ni-Sn alloy layer to the aluminium workpiece, such as the cladding of a brazing sheet product, is fairly good, but may be further improved by a proper pre-treatment of the outersurface of the aluminium workpiece on which the Ni-Sn alloy layer is being deposited, such as the AlSi-alloy clad layer of a brazing sheet product. The pre-treatment comprises a preliminary cleaning step during which  
10   the surface is made free from grease, oil, or buffing compounds. This can be accomplished in various ways, and can be done amongst others by vapour degreasing, solvent washing, or solvent emulsion cleaning. Also a mild etching may be employed. Following the preliminary cleaning, the surface should preferably be conditioned. Several methods can be applied successfully, such as, those set out in  
15   the international application WO-01/88226 of J.N. Mooij *et al.*, incorporated herein by reference, on page 9, line 29 to page 10, line 21.

Furthermore, the present invention is embodied in the use of this NiSn alloy pyrophosphate plating bath as set out above for the electrodeposition of a layer of nickel-tin alloy on the outersurface of an aluminium workpiece, preferably a brazing  
20   sheet product, for the manufacturing of Ni-plated products for use in a fluxless CAB brazing operation.

The invention further provides an assembly of components, for example a heat exchanger, typically for automotive applications, or a fuel cell, typically an electrochemical fuel cell, joined by brazing, whereby at least one of said components  
25   being the brazing sheet product or the brazing product obtained by the method set out above. The brazing operation is preferably carried out in an inert atmosphere (CAB) in the absence of a brazing flux material or under a vacuum.

In an embodiment there is provided a brazed assembly wherein at least one of the components to be joined by brazing is produced by the method in accordance  
30   with the invention described above, and at least one other component is made of steel, aluminized steel, stainless steel, plated or coated stainless steel, bronze, brass, nickel, nickel alloy, titanium, or plated or coated titanium.



- 11 -

## EXAMPLE

On a laboratory scale tests were carried out on aluminium brazing sheets manufactured from an AA3003 core alloy roll clad on both sides with an AA4045 clad alloy, and having a total thickness of 0.5 mm and a clad layer thickness of 50 microns on both sides. The following sequential pre-treatment steps have been used for each sample:

- cleaning by immersion for 180 sec. at 50°C in ChemTec 30014 (a commercial available bath), followed by rinsing,
- 10 - alkaline etching for 20 sec. at 50°C in ChemTec 30203 (a commercial available bath), followed by rinsing,
- desmutting for 60 sec. at room temperature in an acidic oxidising solution, typically 50% nitric acid, followed by rinsing,
- zincate immersion using ChemTec 19023 (a commercial available zincate bath) for 60 sec. at room temperature resulting in a thin zinc layer having a thickness of about 30 nm, followed by rinsing.

Following the above pre-treatment on both sides a Ni-Sn alloy layer had been electroplated of variable tin-concentration using a pyrophosphate bath. The plating operating conditions were a pH of 8, a current density of 1A/dm<sup>2</sup> and a plating bath temperature of 50°C. The pyrophosphate plating bath composition was as follows, with the balance of water:

- 30 g/l NiCl<sub>2</sub>.6H<sub>2</sub>O (0.125 M)
- four different levels of SnCl<sub>2</sub>.2H<sub>2</sub>O
- 165 g/l K<sub>4</sub>P<sub>2</sub>O<sub>7</sub> (0.5 M)
- 25 20 g/l glycine

The Sn-concentration was varied to four different levels in order to vary the resultant tin-concentration of the applied Ni-Sn alloy layer (see also Table 1). The measured tin and nickel concentration in the plating baths have been measured using ICP (Induced Coupled Plasma). Also the nickel and tin concentrations in the resultant electroplated layer have been measured using ICP and given in Table 1.

For the assessment of the post-braze corrosion resistance, the samples have been subjected to a simulated brazing cycle. The samples were heated under flowing

nitrogen, with heating from room temperature to 580°C, dwell time at 580°C for 2 minutes, cooling from 580°C to room temperature. All samples had an excellent brazeability. Following the brazing cycle four samples of each type of plated brazing sheet have been tested in a SWAAT until the first perforations expressed in days of testing appear according to ASTM G-85, and the average results are given in Table 2. The dimensions of the samples for the SWAAT-test were 100mx50mm.

As a reference it is mentioned that typically aluminium brazing sheets manufactured from an AA3003 core alloy clad on both sides with an AA4045 clad alloy, and having a total thickness of 0.5 mm and a clad layer thickness of 50 microns each and devoid of any further metal layers have a SWAAT-test performance of more than 16 days without perforations after being subjected to the same simulated brazing cycle as the examples according to the invention.

As a further reference material also brazing sheet product (same core and clad layer composition and thickness) with a thin zinc bonding layer and only a NiBi-alloy electroplated layer manufactured according to the example of the international PCT application no. WO-01/88226, of J.N. Mooij *et al.*, and incorporated herein by reference, has been tested for its corrosion performance after being subjected to the same simulated brazing cycle as the examples according to the invention.

This example shows how an electroplated nickel-tin alloy layer, and which is lead-free, can be applied on an aluminium workpiece, viz. an aluminium brazing sheet product, and achieving an excellent brazeability. And from the results of Table 2 it can be seen that by increasing the amount of tin with respect to the amount of nickel an improved post-braze SWAAT-test performance is obtained compared to the same brazing sheet product plated only with a known nickel layer comprising a small amount of bismuth to improve the flowability during the brazing operation. Tin may also reduce the surface tension of the molten metal filler during the brazing cycle and thereby improves the flowability of the molten filler metal. The amount of tin to improve the post-braze corrosion performance is by far sufficient to overcome the need for the addition of bismuth or antimony or magnesium added for the same purpose of reducing the surface tension. The combined addition of Sn with Bi and/or Sb and/or Mg remains still possible.

Having now fully described the invention, it will be apparent to one of ordinary

- 13 -

skill in the art that many changes and modifications can be made without departing from the spirit or scope of the invention as hereon described.

**Table 1.** The variable tin concentration in the plating bath and the composition of the resultant plated nickel-tin alloy layer.

Example	Plating bath			Resultant Ni-Sn alloy layer		
	Added SnCl <sub>2</sub> ·2H <sub>2</sub> O (g/l)	ICP Sn-ion (g/l)	ICP Ni-ion (g/l)	Ni (g/m <sup>2</sup> )	Sn (g/m <sup>2</sup> )	Mol- ratio Ni:Sn
1	1.1	0.58	7.57	3.85	0.77	10 : 1
2	2.2	1.14	7.50	3.30	1.32	10 : 2
3	3.3	1.67	7.37	3.39	2.11	10 : 3.1
4	4.4	2.17	7.21	3.48	2.67	10 : 3.8

**Table 2.** Post-braze corrosion performance of the example according to the invention and the comparative examples.

Example	Mol-ratio Ni:Sn	Average SWAAT-test Result (days)
1	10 :	6
2	10 :	7
3	10 :	8
4	10 :	8
NiBi	-	4
Standard AA3003 with AA4045	-	16

- 14 -

## CLAIMS

1. A brazing sheet product comprising a core sheet, on at least one side of said core sheet a clad layer of an aluminium alloy comprising silicon in an amount  
5 in the range of 4 to 14% by weight, and further comprising on at least one outersurface of said clad layer a plated layer of nickel-tin alloy, such that the clad layer and all layers exterior thereto form a metal filler for a brazing operation and having a composition with the proviso that the mol-ratio of Ni:Sn is in the range of 10:(0.5 to 9).
- 10 2. A method of manufacturing an Al or Al alloy workpiece, which method comprises the steps of (a) providing an Al or Al alloy workpiece, (b) pre-treating of the outersurface of the Al or Al alloy workpiece, and (c) plating a metal layer comprising nickel onto said outersurface of the Al or Al alloy  
15 workpiece, characterised in that during step (c) said metal layer comprising nickel is deposited by plating a nickel-tin alloy using an aqueous plating bath comprising a nickel-ion concentration in a range of 2 to 50 g/l and a tin-ion concentration in the range of 0.2 to 20 g/l.
- 20 3. A method according to claim 1, wherein during step (c) the electroplated layer has a composition such that it meets the proviso that the mol-ratio of Ni:Sn is in the range of 10:(0.5 to 9).
- 25 4. A method according to claim 3, wherein taken together said aluminium base substrate and all layers exterior thereto form a metal filler for a brazing operation and having a composition comprising at least, by weight percent:  
Si in the range of 5 to 12 %,  
Ni in the range of 0.03 to 8%,  
Bi in the range of at most 0.3%,  
30 Sb in the range of at most 0.3%,  
Sn in the range of 0.01 to 7%,  
Zn in the range of at most 0.3%,

- 15 -

Mg in the range of at most 5%,  
balance aluminium and inevitable impurities,  
with the proviso that the mol-ratio of Ni:Sn is in the range of 10:(0.5 to 9).

- 5 5. A method according to any one of claims 2 to 4, wherein the workpiece is a  
brazing sheet product comprising a core sheet coupled on at least one surface  
of said core sheet to an aluminium clad layer, the aluminium clad layer being  
made of an aluminium alloy comprising silicon in an amount in the range of 4  
to 14% by weight, and wherein during step (b) at least the outersurface of the  
10 aluminium clad alloy is being pre-treated.
6. Use of an aqueous plating bath in the method according to any one of claims 2  
to 5 for the electrodeposition of a layer of nickel-tin alloy on an Al or Al alloy  
workpiece for the manufacturing of Ni-plated products, preferably a brazing  
15 sheet product, for use in a fluxless CAB brazing operation, the aqueous bath  
having a pH in the range of 6.5 to 9.0, and comprising
- (i) Ni ions in the range of 2 to 50 g/l.,  
(ii) Sn ions in the range of 0.2 to 20 g/l,  
(iii) Sodium pyrophosphate or potassium pyrophosphate in the range of 0.2 to  
20 2 M/l, (iv) a complexing agent, preferably in the form of an  $\alpha$ -amino acid,  
and a balance of water, and preferably in that it is substantially free of lead  
ions.
7. An assembly of components joined by brazing, at least one said components  
25 being a brazing sheet product according to claim 1, or the product obtained by  
the method according to any one of claims 2 to 5.

**ABSTRACT**

The invention relates to a brazing sheet product comprising a core sheet, on at least one side of said core sheet a clad layer of an aluminium alloy comprising silicon in an amount in the range of 4 to 14% by weight, and further comprising on at least one outersurface of said clad layer a plated layer of nickel-tin alloy, such that the clad layer and all layers exterior thereto form a metal filler for a brazing operation and having a composition with the proviso that the mol-ratio of Ni:Sn is in the range of 10:(0.5 to 9). The invention further relates to a method of manufacturing an Al or Al alloy workpiece, which method comprises the steps of (a) providing an Al or Al alloy workpiece, (b) pre-treating of the outersurface of the Al or Al alloy workpiece, and (c) plating a metal layer comprising nickel onto said outersurface of the Al or Al alloy workpiece, and wherein during step (c) said metal layer comprising nickel is deposited by plating a nickel-tin alloy using an aqueous plating bath comprising a nickel-ion concentration in a range of 2 to 50 g/l and a tin-ion concentration in the range of 0.2 to 20 g/l.